

# Fuel Quality: Challenges to the Sustainable Development of Automobile Transport and Approach to Solution

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**Abstract.** The current obstacles to the sustainable development of the vehicle fleet present one of the most serious and complex challenges for technogenic civilization in view of the consumption of rapidly depleting oil and gas resources and the increasing emissions of the products of fuel combustion. The aim of this paper is to study and discuss the impact patterns of the quality of fuel on the environmental and performance characteristics of vehicles and to develop an approach towards improving the quality of fuel as a means of increasing the sustainability of vehicles. The patterns of influence of the chemical composition of the fuel on the temperature conditions in the engine, the emissions of toxic substances and carbon dioxide from the fuel's combustion, the toxicity of the gasoline vapor, carbonization, fuel consumption, engine power and the requirements for a gasoline octane rating have been identified. The use of a fuel additive has been proposed which improves fuel injection in the engines and excludes tarry deposits in the fuel system through the effective detergency and catalyzes the gasification reactions in the engine. The developed fuel additive was shown to have a positive effect by significantly reducing fuel consumption and toxic emissions and improving the performance of vehicles.

## 1 Introduction

Environmental problems associated with the operation of motor vehicles present one of the greatest challenges of human development at the present time. The high concentration of vehicles in cities directly increases pollution of the air through the toxic substances contained within exhaust gases: carbon monoxide, nitrogen, hydrocarbons, including the most carcinogenic one – benzo( $\alpha$ )pyrene, and soot.

Due to the rapid growth of a world vehicle fleet adapted to liquid petroleum fuels, their consumption is also continuously increasing. The solution to the serious environmental threat posed by traditional fuels and combustion products requires a systematic approach.

One of the elements of a technical culture of operation of the vehicles fuelled by liquid petroleum fuel is the use of additives for various purposes [1–5]. For developing countries that are unable to invest substantially in the refining industry the use of additives for fuels

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is the optimal way to rapidly improve the environmental and operational characteristics of vehicles. However, in developed countries, in some cases the use of additives is the only way to maintain optimal engine operation under normal operating conditions.

The proposed study of the impact of fuel quality on the operational and environmental characteristics of vehicles allows the authors to build a concept for the fuel additive which could provide a significant increase in vehicle sustainability.

## 2 Influence of chemical composition of fuel on the temperature regime in the engine and carbon dioxide emissions

Table 1 presents the lower heating value  $Q_l$  for hexane, n-hexene-1, cyclohexane and benzene, according to the reference data [6]. The data show that the heating value per liter of hydrocarbon is the highest for benzene. It should be noted that the calorific capacity per kilogram of aromatic hydrocarbons is lower than that for aliphatic hydrocarbons due to the greater density of the former. Neglecting dissociation of  $\text{CO}_2$  and oxidation of  $\text{N}_2$ , one considers that all the heat released during the adiabatic combustion of hydrocarbon is consumed for heating  $\text{N}_2$ , contained in the fuel-air mixture, and the reaction products –  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The temperature rise during the combustion of the  $\text{C}_n\text{H}_{2n-x}$  hydrocarbon in a stoichiometric mixture with air can be determined by the equation (1):

$$\Delta T = \frac{Q_l}{\sum m_i c_i}, \quad (1)$$

where  $m_i$  – number of moles of the combustion product,  $c_i$  – related heat capacity.

Using the reference data [6] on the average heat capacity for  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  equal to 56, 45 and 33 J/mol · K, respectively, one can obtain:

$$\sum m_i c_i = 56n + 45(n - 0.5x) + 33 \cdot 3.76(1.5n - 0.25x) = 287n - 53.5x. \quad (2)$$

Then, the temperature rise can be calculated by the equation (3):

$$\Delta T = \frac{Q_l}{(287n - 53.5x) \cdot 10^{-3}} \quad (3)$$

The results of calculations shown in Table 1 reveal that the temperature rise of the products of adiabatic combustion of hydrocarbons at the given number of carbon atoms increases with the degree of hydrocarbon unsaturation and is maximal for benzene. Maximal temperature rise attained during combustion results in increased engine power, however it makes greater demands on the anti-knock characteristic of the gasoline [7].

The greater is the density of the hydrocarbon combusted, the greater is the specific release of carbon dioxide per weight or volume unit of fuel [8–10]. The data presented in Table 1 characterize the specific carbon dioxide emissions per unit of energy produced

by the combustion of hydrocarbon,  $\frac{G_{\text{CO}_2}}{Q_l}$ , mg/kJ. Maximal value of  $\frac{G_{\text{CO}_2}}{Q_l}$  was found for benzene.

**Table 1.** Lower heating value of adiabatic combustion, maximal temperature rise for the combustion products and specific carbon dioxide emissions for some C<sub>6</sub> hydrocarbons

Hydrocarbon	Lower heating value $Q_l$ , kJ/l	Maximal temperature rise for the combustion products $\Delta T$ , K	$\frac{G_{CO_2}}{Q_l}$ , mg/kJ
Hexane	30,170	2,150	67.2
n-Hexene-1	30,517	2,215	69.3
Cyclohexane	34,515	2,160	70.8
Benzene	36,390	2,280	82.7

Thus, increasing the content of unsaturated hydrocarbons in the fuel simultaneously with toughening the engine temperature regime increases the specific carbon emissions during engine operation.

3 Toxicity of gasoline

The known Raoult-Dalton relation for ideal mixtures defines the concentration of substances in vapors in equilibrium with the liquid as the following:

$$y = \frac{P}{\pi} x,$$
 (4)

where  $y$  – mole concentration of a substance in vapors,  $x$  – mole fraction of the substance in liquid,  $P$  – saturated vapor pressure of the substance at the given temperature,  $\pi$  – total vapor pressure.

If the concentration of a component with molecular weight  $M_2$  in the gasoline with average molecular weight  $M_1$  is equal to  $x$  wt % and its vapor pressure at a temperature  $T$  is equal to  $P$  kPa, the concentration of saturated vapor of this component of the gasoline can be determined according to the equation (5):

$$C_i = \frac{x / M_2}{x / M_2 + (100 - x) / M_1} \cdot \frac{P}{101.3} \cdot \frac{M_2 \cdot 273}{22.4 \cdot T} \cdot 10^6 \text{ }_{M2} / \text{ }_M^3$$
 (5)

The vapor toxicity of a given gasoline component can be characterized by  $C_i/MAC_i$  ratio, where  $MAC$  is the maximal allowable concentration, while the total vapor toxicity of a multi-component gasoline mixture is equal to  $\sum C_i/MAC_i$ .

Table 2 shows the results of calculation of the toxicity of vapors of n-hexane and its binary mixtures with n-hexene-1, cyclohexane and benzene, made on the base of the average daily  $MAC$  values stated in Russia.

**Table 2.** Vapor toxicity of n-hexane\* and its mixtures with the second component (at 101.3 kPa, 30°C)

Component	Vapor pressure, kPa	Component concentration in vapors mg/m <sup>3</sup>	Vapor toxicity	
			in $MAC$ units	relative to hexane
–	25.43	868,375	57,890	1.00
component concentration in a mixture with hexane of 1 wt %				
n-Hexene-1	30.96	10,565	181,5930	3.14
Cyclohexane	16.20	5,530	61,250	1.06
Benzene	15.91	5,420	111,485	1.93
component concentration in a mixture with hexane of 5 wt %				
n-Hexene-1	30.96	52,800	676,070	11.68
Cyclohexane	16.20	27,615	74,660	1.29

Benzene	15.91	25,990	314,740	5.44
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\*average daily *MAC* for the atmospheric air at the settlements for n-hexane is taken to be equal to 15 mg/m<sup>3</sup>

The data show that at the same content in the mixture n-hexene-1 and benzene heighten the toxicity of the vapors to the greatest extent. Note, however, that benzene is very stable under normal conditions and practically does not enter into chemical reactions, while n-hexene-1 is sufficiently rapidly oxidized with oxygen in the air and removed from the atmosphere. In view of this, benzene is the least desirable component of the gasoline and limiting its content in a fuel set to no more than 1 vol. % by current European standards EN 228:2012 as well as by the Worldwide Fuel Charter [11] is quite justified. It should be noted that motor transport is a source of 80–90% of benzene in the atmosphere [12–14]. Oxidation products of benzene in the body, especially phenols and polyphenols, have a toxic effect and disrupt enzymatic processes in the cells and cause severe poisoning of the body or even death. Oxidation of benzene homologs leads to the formation of less toxic compounds.

To reduce losses from evaporation of gasoline and its negative environmental and economic consequences the saturated vapor pressure of gasoline should be limited. Essentially, with no change in chemical composition, the saturated vapor pressure of the gasoline can be reduced by introducing into it a surfactant additive which reduces the percentage of gasoline in the surface layer [3, 4].

4 Carbonization and its impact on environmental and performance characteristics

During the process of vehicle operation carbon is deposited on the cylinder walls and the pistons. Aromatic hydrocarbons possess the greatest propensity for forming carbon deposits. The authors investigated the dependence of pyrocarbon formation in the pyrolysis of individual hydrocarbons in an inert carrier on the chemical structure of the hydrocarbons. At a temperature of 1123 K the rate of the pyrolytic carbon formation from benzene is 7 times higher than that from cyclohexane.

Condensed (polycyclic) aromatic hydrocarbons are the precursors of carbon deposit during its formation. Benzene, as well as other aromatic hydrocarbons, has the highest propensity to form benzo(α)pyrene compared to hydrocarbons of other classes [15–17].

Table 3 illustrates the impact of hydrocarbons on the content of benzo(α)pyrene in exhaust gases. It is seen from the data presented that at the same number of carbon atoms alkanes and cycloalkanes give amount of benzo(α)pyrene which is, by the order of magnitude, smaller than that given by benzene.

**Table 3.** Concentration of benzo(α)pyrene in exhaust gases during combustion of hydrocarbons (excess air coefficient is 1.15)

Hydrocarbon	Concentration of benzo(α)pyrene in exhaust gases, ppm
Hexane	1.0
n-Hexene-1	1.0
Cyclohexane	1.1
Benzene	28.6

At peak temperature concentrations of carbon and nitrogen oxides formed during the fuel combustion in the engine are maximal and futher decreasing the temperature “freezes” the concentrations of the gases formed [4]. Thus, according to estimates for the formation of nitric oxide from nitrogen and oxygen within the air, when decreasing

the temperature from 2500 to 2000 K the reaction rate decreases by a factor of  $2.2 \cdot 10^6$  and the equilibrium concentration of nitrogen oxide reduces by a factor of 7.1. When the temperature drops from 3000 to 2000 K, the equilibrium concentration of carbon monoxide at a pressure of 1 MPa in the products resulting from the combustion of hydrocarbons in oxygen reduces from 23 to 18 vol. %.

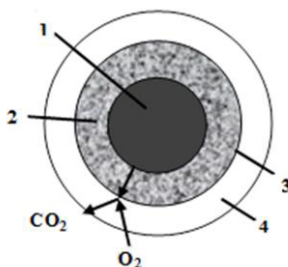
Since an increase in the content of unsaturated and aromatic hydrocarbons in the fuel toughens the temperature conditions in the engine due to both the higher temperature developed during combustion and increased carbon deposits formation, which hinders the process of heat-removal through the wall, the greater the degree of unsaturation of the fuel is, the greater are the emissions of oxides of carbon and nitrogen during the vehicle operation.

As the carbon deposits form, the friction force between the piston and the cylinder sharply increases and this increases fuel consumption. Another reason for increasing fuel consumption is the emergence of so-called “surface ignition” – preignition which leads to an increase in pressure of the gaseous mixture in the compression stroke as a result of the reaction heat release. This increases the energy consumption for compression and results in loss of engine power. In addition, the low thermal conductivity of carbon deposit leads to an increased temperature of fuel combustion [3, 4, 7, 18, 19], which increases the requirements for the anti-knock resistance of the gasoline. Deterioration of heat removal from the combustion chamber due to increased carbonization results in an increase in temperature when exhaust gas is released, which may lead to burnout of exhaust valves.

## 5 Soot emissions

The micro-diffusion combustion of fuel in diesel engines results in the formation of soot, the emission of which is a significant environmental problem.

Figure 1 shows a model of combustion of droplets of diesel fuel in an engine. Fuel vapors diffuse to the flame front continuously heating. A deep pyrolysis of fuel molecules occurs and soot particles form. Some of the soot particles passing through the front flame burn out. However, the passing time for the largest particles is not enough to burn and they are emitted with the exhaust gases. The soot output increases as the C:H ratio in the fuel increases [20–22] and so too does the fuel density and the content of heavy fractions. The highest soot output is due to thermal decomposition of bi- and tricyclic aromatic hydrocarbons; monocyclic aromatic hydrocarbons give lower output and alkanes and cycloalkanes – even less.



**Fig. 1.** Scheme of diesel droplet's combustion: 1 – liquid, 2 – vapor layer, 3 – combustion zone, 4 – layer of oxygen and carbon dioxide diffusion and afterburning.

Since soot formation increases with an increase in aromaticity and the molecular weight of the aromatic hydrocarbons, regulation of the polycyclic aromatic hydrocarbons' content

in the diesel fuel is necessary and justified. The following ways to reduce soot emissions from diesel engines are possible:

1. Decreasing the formation of soot particles. This can be achieved by increasing the total surface of the fuel droplets. As a result of this the rate of evaporation of the fuel increases and droplets' residence time in the preflame zone reduces. The work of spraying consists of the work done during the injection to overcome aerodynamic resistance and the work to create a new surface equal  $\sigma S$ , where  $\sigma$  – the surface tension on the fuel/air boundary,  $S$  – total surface of the droplets. At the constant aerodynamic resistance a reduction in surface tension leads to an increase in the total surface of the fuel droplets.

2. Increasing the degree of combustion of soot particles. This is possible if the soot particles will comprise a carbon gasification catalyst.

## **6 Increasing sustainability of automobile transport by means of a multifunctional additive for fuels**

### **6.1 The concept of the additive providing improved sustainability of vehicles**

To reduce carbonization in an engine with the appropriate temperature mitigation conditions in the engine, to decrease toxicity of exhaust emissions and fuel consumption it is necessary to improve fuel spraying, which can be achieved by introducing a surfactant that lowers the surface tension of the fuel droplets at the interface with air. Preventing the non-evaporable fuel droplets from being reached the wall will minimize carbonization. Improved spraying will reduce soot formation in diesel engines as well.

The introduction into the engine, along with the fuel, an element which could provide catalysis for gasification reactions, will not only contribute to the elimination of carbon deposition and soot burnout, but also greatly reduce emissions of products of incomplete oxidation and condensation of hydrocarbons of the fuel, including polycyclic aromatic hydrocarbons.

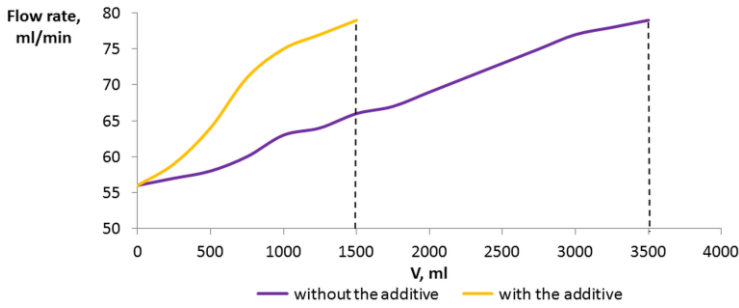
For regular engine supply with the gasoline, it has to possess high detergency to prevent occurrence of tarry substances in the gasoline pipeline. It can be achieved by introducing a surfactant. Reduction of losses of the gasoline from evaporation may also be achieved due to the surface-active effect of the additive introduced.

Thus, to achieve the desired integrated effect of improvement to both the environmental and operational characteristics of vehicles the additive should combine the properties of the surfactant and the gasification catalyst.

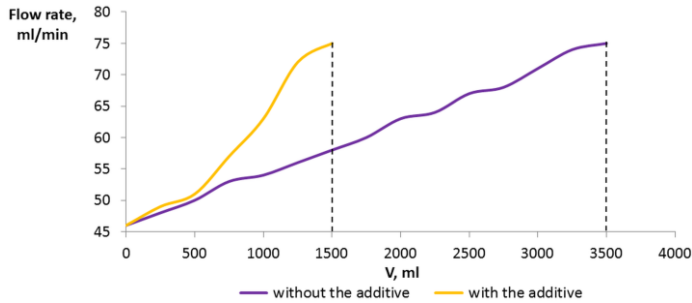
### **6.2 Results of the influence of the versatile additive on the properties of fuels**

The authors have developed a versatile additive for gasoline and diesel fuels with a high surface activity, containing within the structure an effective catalyst for gasification reactions. The additive can be applied to the fuel in ultra-small concentrations: 9.25 mg per 1 kg of gasoline and 27.75 mg per 1 kg of diesel fuel.

The developed additive significantly increases the detergency of fuels. The results of the additive's influence on detergency are shown in Figure 2. Introduction of the additive into gasolines reduces the saturated vapor pressure by 15–20% which leads to a decrease in gasoline loss due to evaporation of 17–30%.



(a)

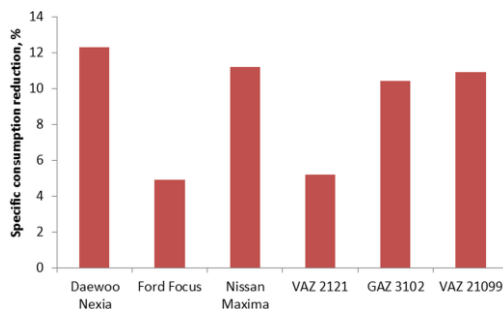


(b)

**Fig. 2.** Influence of the additive on the detergency of fuels: (a) gasoline (concentration of the additive is 9.25 mg/kg); (b) diesel fuel (concentration of the additive is 27.75 mg/kg).

The additive significantly reduces carbonization due to improved fuel spraying and catalyzes the gasification reactions of polycyclic aromatic hydrocarbons (PAH), including benzo( $\alpha$ )pyrene, and carbon deposit. As a result, PAH emissions are reduced by up to 95% and carbon deposits are removed almost completely.

Enhancing heat-removal through the wall by eliminating carbon deposit facilitates the combustion process in the engine and reduces emissions of gaseous toxic substances: nitrogen oxide emissions reduce by 20.6% in a diesel engine and by 26.5% in a gasoline engine, CO emissions drop to 14.6% (depending on the excess air coefficient). Increased completeness of combustion of hydrocarbon fuels results in emissions reducing by 35.5–37.2%. Eliminating carbonization reduces the non-productive power expenditure and leads to a reduction in gasoline consumption by 10–12% (Figure 3), diesel fuel – by 5–7%. As a result, a reduction in the specific fuel consumption leads to a corresponding decrease in carbon dioxide emissions. Elimination of carbon deposit formation in the engine reduces the requirements for gasoline octane number by 7–12 points.



**Figure 3.** Influence of the additive on the gasoline specific consumption.

Due to the surface-active influence of the additive, which improves the fuel spray process, combined with its catalytic effect, soot emissions are reduced significantly. In the diesel engine Zil-64 bench test a reduction of soot in the exhaust gases of the engine at maximum load was 50% (from 0.36 to 0.18 mg/l). Thus, the developed versatile additive exhibits effectiveness for both gasoline and diesel fuels, improving the environmental and operational characteristics of fuels concurrently.

## 7 Conclusion

Patterns of influence of the chemical composition of fuels on the environmental and operational characteristics of vehicles were identified. An increase in the content of aromatic hydrocarbons was shown to lead to a toughening of the temperature regime in the engine due to both a rise in the maximum temperature of fuel combustion and to increased carbonization. As a result, the specific consumption of fuel, emissions of toxic substances, soot and greenhouse gases increase. Moreover, this also increases the requirements for the octane number of gasoline consumed.

Therefore, measures are needed to reduce the content of aromatic hydrocarbons in fuels which requires the development of hydrocracking and hydrotreating capacities in refining industry.

A concept was formulated for a fuel additive which provides an opportunity to increase sustainability of automobile transport due to the integrated positive influence on the fuel's properties. The additive, combining the properties of a surfactant and a catalyst for gasification reactions, greatly improves the environmental properties of fuels, reducing their specific consumption, gasoline loss from evaporation and reduces the need for high-octane gasolines. Use of the additive can significantly mitigate the negative impact of the high content of aromatic hydrocarbons in fuels which is a serious issue for a number of developing countries.

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